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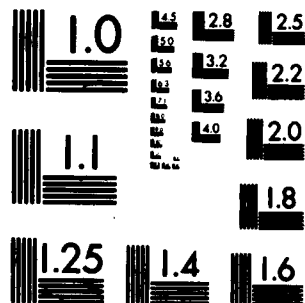
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Anomalous Components of Supercooled Water Expansivity, Compressibility
and Heat Capacity (C_p and C_v) from Binary Formamide + Water Solution Studies

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however, yields a "normal" component which is large compared with that estimated from ethanol-water solutions and leads to very poor fits to critical point equations. The source of this discrepancy is discussed. Combining all results, we have obtained a plot of C_v for binary solutions at different temperatures, and thereby have estimated an anomalous component for the constant volume heat capacity. In contrast to the constant pressure heat capacity, which diverges, the constant volume anomalous component behaves like a Shottky anomaly. In this respect an analogy with the adiabatic compressibility may be noted.



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ANOMALOUS COMPONENTS OF SUPERCOOLED WATER EXPANSIVITY, COMPRESSIBILITY
AND HEAT CAPACITY (C_p and C_v) FROM BINARY FORMAMIDE + WATER SOLUTION STUDIES

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Abstract

Following heat capacity studies of $\text{H}_2\text{N}_2 + \text{H}_2\text{O}$ and $\text{H}_2\text{O}_2 + \text{H}_2\text{O}$ solutions from which an anomalous component of the pure water behavior could be extracted by extrapolation, we extend this type of study to a system which has the chemical stability needed to permit expansivity and compressibility measurements as well. Data accurate to $\pm 2\%$ on each of these properties as well as of the heat capacity are reported. The expansivity data support almost quantitatively an earlier speculative separation of the bulk and supercooled water expansivity into a "normal" part and an "anomalous" part, the latter part fitting a critical law $\alpha_{\text{anom}} = A(T/T_g - 1)^{-\gamma}$ with exponent $\gamma = 1.0$. According to the present analysis, the excess expansivity which is always negative, yields T_g in the range 225-228, γ in the range 1.28-1.0, depending on the choice of background extrapolation function. The background contribution to the heat capacity obtained from the present work is intermediate in character to that from the previous two systems and leads to similar equation parameters. The background contribution to the compressibility on the other hand is very different from that speculated earlier by Kanno and Angell and approximately verified by recent studies on ethanol-water solutions by Conde et al.⁽¹⁾ The

background component from the present analysis is $\sim 50\%$ larger, with the result that the excess or anomalous component, at least when values above 0°C are included in the analysis, cannot be sensibly fitted to the critical point equation. The possible origin and interest content of these differences is discussed. Combination of the new thermodynamic data permit estimation of C_v values for the solution, and by extrapolation, a "normal" C_v component for water. The "anomalous" component of C_v for pure water obtained by difference has the form of a Shottky anomaly, in contrast with the corresponding C_p component which diverges.

ANOMALOUS COMPONENTS OF SUPERCOOLED WATER EXPANSIVITY, COMPRESSIBILITY
AND HEAT CAPACITY FROM BINARY FORMAMIDE + WATER SOLUTION STUDIES

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Introduction

Recently, in an attempt to elucidate the origin of the many anomalies found in the behavior of supercooled water, we reported investigations of the heat capacity of binary solutions of water with the water-like second components, hydrazine and hydrogen peroxide.⁽²⁾ The object of the studies was to obtain data from binary solution regions in which the anomalies characteristic of pure water had been eliminated, so that extrapolations back to pure water would yield an estimate for the "normal" component of the total water heat capacity, thereby permitting the magnitude of the "anomalous" component to be extracted.

Although the "normal" component obtained from the two binary systems was not unique, the "anomalous" component thereby obtained showed a temperature dependence which conformed well to a critical point type of equation

$$C_{p, \text{anom}} = A(T/T_s - 1)^{-\gamma} \quad (1)$$

with a singularity temperature, T_s , of 225 ± 1.5 K and "critical" exponents γ either side of the value of unity, depending on the background component used. The singular temperature is in good agreement (approximately 3° below) the

value assigned to T_g from the fits of total supercooled water properties to the same equation in previous analyses of the low temperature anomalies.

Significantly, it lies just a few degrees below the lowest temperature to which water in the purest condition and smallest particles yet studied can be cooled without crystallization occurring, a finding for which different interpretations have been advanced. (3-5)

It is clearly desirable to determine the extent to which these observations can be confirmed by analysis of similarly separated anomalous components for the other intensive thermodynamic variables, expansivity and compressibility. Unfortunately neither of the previously studied binary systems is easily investigated in the supercooled regime using simple dilatometric technique developed earlier for supercooled water studies, because the second component is inherently unstable and the solutions decompose in the presence of the mercury marker bead used in the volumetric analysis. We have, therefore, sought a third system in which this problem would not arise and in which all three thermodynamic properties could be studied for mutual comparison.

Hydroxylamine, NH_2OH , is an appealing possibility because it has the same lone pair:proton ratio as water, in contrast with H_2O_2 (4:2) and N_2H_4 (2:4). However NH_2OH , like H_2O_2 and N_2H_4 , lacks stability and therefore was not chosen. After consideration of several possibilities we decided on formamide NH_2CHO which, in addition to being stable, seems to form rather ideal solutions with water. The m.p. -5°C , b.p. 125°C and dielectric constant $\epsilon = 55$, are all comparable with water. No compounds form in this system unlike the case with H_2O_2 and N_2H_4 . Both ends of the NH_2CHO molecule participate in H-bonding and the lone pair:proton ratio 3:2 is close to that of water. Their distribution, also, is not completely incompatible with the open bonding of water since the partial molar volume of water in the binary system is only slightly less than

that of pure H_2O across the entire binary system.⁽⁶⁾

We have succeeded in obtaining data of good quality for each of the three thermodynamic properties for solutions at 20 mol % intervals across the composition variable. This paper reports the results of these measurements, and their analysis. We have also studied a transport property, the viscosity, but will report the results of that work separately. Our results for the compressibility make interesting comparison with the current findings of Conde et al for ethanol + water solutions obtained by light scattering measurements.⁽⁷⁾

Experimental

The NH_2CHO used was Reagent grade. DSC fusion analysis for water content (described in our previous paper) showed the presence of 0.25 mol % H_2O , which was allowed for in all solution preparations. H_2O used was deionized triply distilled, and solutions were prepared by simple weighing procedures.

The heat capacity of the solutions was measured over the temperature range from 25°C down to a low temperature limit determined by solution freezing. The lowest temperatures reached were 210 K for the 30 and 40% NH_2CHO solutions. The careful sectional baseline determinations which made 1% accuracy measurements possible in our previous work,⁽⁷⁾ were again utilized, and results of better than 1% precision were consistently obtained.

Expansivities were measured in the stable solution temperature region by using a dilatometer made of precision bore capillary (≈ 2 mm in diameter) with a glass bulb attached to one end. The conversion of the meniscus position, read with a cathetometer, into the volume was made, after calibration at 20°C with carefully degassed mercury. The small corrections for pyrex expansivity was made using the literature (CRC Handbook of Chemistry and Physics) value of

$2.5 \times 10^{-5} \text{ K}^{-1}$. The expansivity values calculated from the smoothed volume vs. temperature curve were obtained with an uncertainty of ca. $\pm 1\%$ reproducibly for different series of sample preparation and measurement.

Compressibility measurements were begun by determining absolute values for each solution at 5 MPa and 25°C using a 30 cm long 12 mm precision bore pyrex capillary sample container in which the sample was isolated from the pressure transmitting fluid by a 5 cm Hg slug. The effect of pressure on the internal volume of the capillary vessel was calibrated by making similar measurements in the same vessel on spectroscopic grade benzene to obtain the glass dilativity, d [$d = (1/V) \partial V / \partial P_{\text{internal}} = -(\text{compressibility})$]. The 1 atm pressure volume of the vessel was determined using degassed mercury. To make high pressure and low temperature measurements on these same solutions, the fine capillary mercury bead displacement method of Kanno⁽⁸⁾ was adapted using the above-measured absolute values to determine the effective capillary length. Rather than correct results for the capillary dilation effect as in the earlier measurements, we included the effect of dilation in the length calibration procedure itself by least squares fitting measured bead displacements in the range 0 - 10 MPa to the expression

$$\kappa_T = \frac{l_o d + (l - l_o) d + \frac{\partial(l - l_o)}{\partial P}}{l_o d + (l - l_o)} \quad (2)$$

where κ_T is the accepted compressibility^(9,10) in the known temperature range, $(l - l_o)$ is the difference between the reading of the reference and meniscus points, and d is the glass dilativity. The dilativity thus determined simultaneously with the effective length, was found to be the same, $3.67 \times 10^{-5} \text{ MPa}^{-1}$ within $\pm 10\%$ as that obtained in the benzene calibration series with the precision bore capillary of diameter 1.0 mm. An accuracy of 10% is sufficient

to reduce the error in compressibility due to dilation to less than 0.1%. Values of κ_T obtained for pure water in the range 0 to -20°C were found to be the same as the corrected values reported earlier⁽⁸⁾ to within the 1% uncertainties of the measurement.

Results

Results of heat capacity measurements on the binary solutions in the temperature interval between 290 K and 210 K are presented in Fig. 1. Measurements close to pure water have not been attempted as (a) their general form has been shown in an earlier paper,⁽²⁾ and (b) measurements in the supercooled region, requiring emulsion techniques, are rather tedious.

Comparison of our solution data can be made with previous work by Visser et al⁽⁶⁾ at 298.15 K. Over most of the composition range we find agreement within 1%, which is the uncertainty of our measurements. To estimate the "normal" part of the pure water heat capacity a weakly curvilinear function seems required by the solution data. The curvature is such as to emphasize the extraordinary upswing in C_p as pure water is approached at low temperatures. A crude estimate of the partial molar heat capacity of NH_2CHO at high dilution at -35°C yields the extraordinary value $-900 \text{ J K}^{-1} \text{ mol}^{-1}$, comparable with the value $-850 \text{ J K}^{-1} \text{ mol}^{-1}$ for H_2O_2 quantitatively obtained, but not reported, from our earlier emulsion data on the $\text{H}_2\text{O}_2 + \text{H}_2\text{O}$ system.⁽⁶⁾

Results of the expansivity measurements on the binary solutions are shown in Figs. 2 and 3. Figure 2 shows the raw data for each composition vs. temperature to indicate the precision of the measurement. Note that measurement of α to $\pm 1\%$ requires precision in volume measurement to 1 in 10^6 . Data in Fig. 3 are obtained from best lines through the Fig. 2 points. In this case the relative magnitude of the low temperature anomaly encountered on

approaching pure water is very large, since not only is there a reversal in sign, but the absolute magnitude of the property changes fourfold between 50 and 100% H_2O . As in the case of the solution heat capacity data, the most plausible extrapolation of the binary solution range is a curvilinear one, our best representation of which is shown by the dashed lines at 300, 270, and 240 K in Fig. 3. In the case of the expansivities, there are no literature data with which comparisons can be made.

Results of the compressibility κ_T measurements, in this case reported for 10 MPa are shown in Fig. 3. As in the case of the expansivity data, an influence of the water-water interactions becomes evident at much larger mole fractions of the second component than in the case of the heat capacity data, a point which is discussed further below. Particularly at the higher temperatures, the binary solution behavior is very simple, and the extrapolations to 0% formamide content are fairly unambiguous. Again, there are no literature data with which comparison can be made.

Values of κ_T are also available for high pressures, up to 1500 bar but they will be considered in a separate paper.

Discussion

In Figs. 5, 6 and 7 we show the experimental value of the three derivative properties and the background component obtained from the extrapolated value of the property at $X_{\text{NH}_2\text{CHO}}$ for each isotherm of Figs. 1-3.

In Fig. 5 we include the background C_p functions obtained from similar studies on the $\text{H}_2\text{O}_2 - \text{H}_2\text{O}$, and $\text{N}_2\text{H}_4 + \text{H}_2\text{O}$ systems.⁽²⁾ The present system yields values equal to those from $\text{N}_2\text{H}_4 - \text{H}_2\text{O}$ solutions at high temperatures and values intermediate between $\text{N}_2\text{H}_4 - \text{H}_2\text{O}$, and $\text{H}_2\text{O}_2 - \text{H}_2\text{O}$ -based values at low temperatures due to a smaller temperature dependence than in the $\text{N}_2\text{H}_4 - \text{H}_2\text{O}$

case. This is also the behavior of the "normal" component extracted from LiCl-H₂O solution studies to be reported separately, indicating that some average of the values observed to date lying closer to N₂H₄- than to H₂O₂- based values is the appropriate background.

In the case of the expansivity, Fig. 6, it is possible, with clarity, to show the anomalous part of the expansivity as well as the total and background components from which it is obtained by difference. To check the sensitivity of our treatment to the element of arbitrariness which enters in our extrapolation function, we show "normal" and derived "anomalous" components for three different choices of extrapolation function. This is a more serious problem for the volume derivative properties than for C_p , at least in the present system, because the effect of the water structure is felt out to much larger mole fractions of the 2nd component (compare Figs. 1 and 2). The three backgrounds in Fig. 6 differ in the number of mole fraction points used in the quadratic functions which were extrapolated to $X = 0$. Extrapolation (a) shown in Fig. 3 used 1.0, 0.8, and 0.6 mole fraction of NH₂CHO, extrapolation (b) used these points and also $X(\text{NH}_2\text{CHO}) = 0.4$, while extrapolation (c) used a straight line through the first two points at 0.8 and 1.0 mole fractions of NH₂CHO. We will see below that while this small difference has little effect on the best fit value of T_g in Eq. (1) it has a significant effect on the associated exponent γ . The background suggested by Speedy⁽³⁾ in the absence of any experimental guidance, is identical to (c) shown as a dashed line.

In Fig. 7, we show the total and background components of the compressibility obtained by the straightforward extrapolations of Fig. 4. Included for comparison is the measured compressibility of the simplest diol, ethylene glycol, one of the few other simple molecular liquids with a compressibility smaller than that of water.⁽¹¹⁾ A problem for our subsequent

analysis is seen immediately in the tendency of the background component to become equal to the total compressibility i.e. anomalies vanish, at temperatures as low as 340 K.

The background obtained in the present work is much larger than that assumed (by relation to ethylene glycol) in an earlier analysis of the compressibility anomaly, of water.⁽⁸⁾ It is also larger than the "normal" component for water recently deduced by Conde et al⁽¹⁾ from sound velocity studies on ethanol + water solutions. In the latter system, the anomalous temperature dependence of compressibility is eliminated by addition of just 10 mol % EtOH, whereas obvious anomalies persist even at 35% formamide in the present system. The molecular shapes and sizes of the two second components are rather similar $\text{NH}_2\text{---CH=O}$, and $\text{CH}_2\text{---CH}_2\text{---OH}$, and the difference in behavior must reflect the influence of the hydrogen bonding amine group in formamide in increasing the structural compatibility with water. The suggestion is that formamide may be too compatible with water for our purpose of separating out abnormal fluctuation components, and that the background extracted in our work is therefore an overestimate. The contrast serves to illustrate the severe limitations of the binary solution extrapolation method for separating "anomalous" from "background" contributions to an intensive thermodynamic property. One runs the danger of choosing, as an "appropriate" binary system for background determination the one which finally delivers the "anomalous" component one wants to find.

With this chastening thought in mind, let us observe the temperature dependence of the "anomalous" components of water for the three properties C_p , α and K_T .

We show graphically the tests of Eq. (1) for C_p and α , respectively, in Figs. 8 and 9.

The corresponding plots for the excess κ_T , which cover the smallest supercooling range ($T > -26^\circ\text{C}$), are not shown because the parameters which give the best linear fits are absurd - for instance, $T_g = -100\text{ K}$. Although this sort of result would seem to immediately invalidate our approach we must note that the excess κ_T obtained by Conde et al⁽⁷⁾ from a similar analysis of data obtained on ethanol + H_2O solutions (from light-scattering measurements) fitted Eq. (1) with parameters very similar to those of our present best fits to the excess C_p and α values, viz.⁽⁷⁾ $T_g = 228\text{ K}$, $\gamma = 0.91$. This observation encourages us to look more closely at the dependence of the Eq. (1) parameters for the excess α data on the composition range of binary data used to determine the background component. The point is that C_p , which is determined by entropy fluctuations ($\propto(\Delta S)^2$) seems to become "normal" in solutions of quite small mole fractions of added formamide (Fig. 2), while κ_T , which is determined by volume fluctuations alone ($\propto(\Delta V)^2$), may be "abnormal" across the whole composition range. α , which is determined by the product of density and volume fluctuations, might therefore be expected to show some diagnostically useful trend as the composition range from which the background contribution is assessed, is changed. In Fig. 7 the three best fit lines (a), (b) and (c), are for the excess (anomalous) components of α obtained when successively smaller composition ranges (which successively weaken any residual anomalous water influence) are used in the background determination (see previous section).

Apart from further demonstrating the weakness of our binary solution method for separation of "normal" and "anomalous" components of water properties, this sequence is interesting in that it shows the best fit values of γ_α decreasing from high values to unity as the possibility of residual cooperative water influence is increasingly reduced.

Although this might seem to reinforce the significance of the value 1.0 for γ

suggested in our earlier analyses, an extension of the line of reasoning would imply a smaller value of γ as a possibility to be dealt with. If the persistence of abnormal volume fluctuations across the binary is so influential then C_p data should yield the most reliable separations, hence the most reliable values of γ . C_p data are also available over the widest temperature range and, perhaps marginally, with the greatest accuracy (we have not used data below -35°C because of the difficulty of proving absence of incipient crystallization distortions of the data). The present C_p data yield "normal" component magnitudes very similar to those obtained from an earlier $\text{N}_2\text{H}_4 + \text{H}_2\text{O}$ solution study, but with a smaller temperature dependence (see Fig. 5). These distinctions lead to a value of $\gamma = 0.75$ which is the smallest yet obtained. However, such a small value of γ forces T_g to the correspondingly large value of 230 K which seems improbable. For the N_2H_4 -based C_p background, we earlier obtained $\gamma = 0.93$, $T_g = 226$ K. Without knowledge of the volume derivative properties based on N_2H_4 as a second component we cannot comment on which if either set to favor.

It seems reasonable overall to conclude that if Eq. (1) is to apply to these phenomena then γ values close to, though less than, 1.0 seem the most plausible.

Values close to unity would be in accord with our earlier understanding of mean field theory predictions for approach to a mechanical instability for a liquid (e.g. on superheating),⁽¹²⁾ but it now appears, from analysis by Speedy⁽¹⁴⁾ and earlier work by Compagner,⁽¹⁵⁾ that series expansions around a spinodal point actually require $\gamma_{C_p} = \gamma_\alpha = \gamma_{K_T} = 0.5$. The exponent 1.0 only applies at the critical density and leads to thermodynamic inconsistencies at T_g for other densities. It is not clear, however, how close to T_g the observations must be made for the exponent 0.5 to be observed. We recently

noted⁽⁷⁾ that the Haar-Gallagher equation of state for water⁽¹⁶⁾ gives behavior near the superheated liquid spinodal point which is compatible with an exponent of unity for C_p values in the range of data for supercooled water, but went over to $\gamma \approx 0.5$ behavior when the actual instability temperature, and data very close to it, were used in the analysis. So values of γ near unity from the present study are not incompatible with a spinodal interpretation of the observed anomalies. They are also compatible with the alternative possibility⁽¹⁷⁾ that the anomalies reflect the approach to a higher order transition within the liquid state associated with the establishment of some long-range order in the hydrogen bond network - a notion which has recently been provided with a topological basis by Stanley and Teixeira.⁽⁵⁾

Thus the issue of the origin of the curious behavior of water at low temperatures cannot be settled by these measurements. The difference between the apparently distinct postulates of spinodal (edge of liquid free energy surface) and internal transition (bump on the liquid free energy surface) may not be as great as it seems. Indeed it is not inconceivable that a changeover could occur from one form of behavior to another as pressure is increased sufficiently above 1 atm. One published equation of state⁽¹⁶⁾ hints at this possibility in its predictions of properties well outside its valid range.⁽¹⁸⁾ Such oddities would be a property of the liquid free energy surface and would have nothing to do with the equilibrium between water and ice which can be observed in separate experiments.

Anomalies at Constant Volume

Since the extraordinary nature of low temperature water is clearly dependent on the fluctuations in entropy and volume made possible by the migration of hydrogen bonds between water molecules which continuously attempt to establish a local open tetrahedral network (amorphous ice-like) order,

certain differences in the temperature-dependent properties from those discussed above must be expected when measurements are performed at constant volume or constant entropy. Indeed, the vanishing of the heat capacity divergence and its replacement with a weak maximum when examined at constant volume was reported at the beginning of the current wave of supercooled water studies.⁽¹⁹⁾ Likewise, evidence for a maximum in κ_s has recently been seen in the clever levitated droplet sound velocity measurements of Trinh and Apfel.⁽²⁰⁾ The latter maximum has also been implied by short extrapolation of similar data from recent light scattering studies on EtOH + H₂O solutions in which the κ_s maxima were directly observed.⁽⁷⁾ It is therefore of interest to use the present data to see whether there is an important "anomalous component" to the heat capacity for water when studied at constant volume.

C_v in the range 17 to -35°C can be obtained from the present data using the standard thermodynamic relation

$$C_v = C_p - VT \alpha^2 / \kappa_T \quad (3)$$

The results are shown in Fig. 10. Before commenting on their implications it should be remembered that the values of C_v thus calculated are $(\partial E / \partial T)_v$ at the volume at which C_p is measured, rather than at a single value of volume which is the same for all temperatures. For our main purpose of observing the extrapolation of solution C_v values to pure water, however, this distinction is immaterial, though it affects the form of C_v vs. T shown in the inset to Fig. 10. At a single fixed volume the C_v vs T function will be somewhat sharper, depending on the value of volume held constant.

Figure 10 clearly shows that there is indeed a large contribution (~ 12%) to C_v of pure water from an aspect of water-water interactions which is

eliminated by addition of only 20 mol % of formamide.

This is not surprising: the density and temperature fluctuations will occur whether or not the system can change its volume. It is useful, however, because it allows us to form a clearer idea of the magnitude of the specifically "waterlike" fluctuations which determine C_v for water, and to obtain a form for the "excess C_v " as a function of T which is useful for theoretical purposes (most theories being constructed for constant volume systems). C_p and C_v for pure water, are shown against the "normal" C_v component obtained by the solution extrapolations in the upper insert to Fig. 10.

The values of C_v shown in Fig. 10 are assessed using the most recent measurements of C_p for supercooled water⁽⁷⁾ which revise downward by some 5% at the lowest temperature, the values first reported for this property.⁽¹⁹⁾ The revision has the effect of producing a maximum and a sharp fall-off in C_v at lower temperatures, where previously only a weak maximum had been seen. The point at -35°C (238 K) is quite uncertain, since it depends on combinations of measurements of intensive thermodynamic properties, each of which is difficult to measure with accuracy, and all of which are changing very rapidly with temperature in this region. Furthermore, the value of κ_T used for this point required a 9°C extrapolation of existing data. It seems very improbable that C_v for pure water would fall below the value of the "normal" component assessed in the present work, hence we suggest that the most probable form for C_v is that shown by the dashed line, which approaches the C_v (normal) line asymptotically.

The separated excess C_v due to that component of the mean square temperature fluctuation that is uniquely "water-like", is shown as ΔC_v in the lower insert to Fig. 10. It has the form of a Shottky anomaly which is

predicted by the simple random network "bond lattice" model,⁽²¹⁾ in which H-bonds forming during thermal de-excitation are assumed, in the non-cooperative case, to cause the same volume and energy increments irrespective of their number. In this it differs from the Stanley-Teixeira random bond percolation model⁽⁵⁾ which assigns, very reasonably, an extra volume per bond to the "saturated" clusters of bonds which arise naturally in the course of cooling at constant pressure. A similar idea was briefly described in an earlier paper⁽³⁾ in which it was pointed out that a volume-cooperative modification of the bond lattice model⁽²²⁾ (in which the ΔV per bond is made proportional to the mole fraction of "on" bonds) could qualitatively describe the anomalous compressibility observations for water. Since according to Le Chatelier's principle the formation of large volume bond clusters ("patches")⁽⁵⁾ natural to random bonding systems of H_2O molecules⁽⁵⁾ at low temperatures must be discouraged by a constant volume condition, fixing the system volume must introduce a non-random element into the bond distribution. This is, of course, manifested as an increase in pressure with decreasing temperature at constant volume.

The form of the C_v anomaly is not unlike that of the adiabatic compressibility implied by the sound velocity studies of Trinh and Apfel,⁽²⁰⁾ and of Conde et al⁽¹⁾ referred to above, and the temperatures of their maxima differ by only some 10° . In the H_2O -ethanol solutions of the latter study the κ_g maximum is sharply defined. Temperature and volume fluctuations, which determine C_v and κ_g , are statistically independent,⁽²¹⁾ however, and it is worth remembering⁽³⁾ that the isothermal compressibility ($\propto (\Delta V)^2$) increases almost as rapidly with decreasing temperature at a constant volume of $18 \text{ cm}^3 \text{ mol}^{-1}$ as it does at a constant pressure of 1 atmosphere.

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Figure Captions

Figure 1 Expansion coefficients for water-formamide solutions as a function of temperature. Each point is determined from column length measurements taken ≈ 2.5 K apart in temperature. Points at $X_{\text{NH}_2\text{CHO}} = 0.40$ represent two different runs, there being more scatter at this composition than at others. (Note $\pm 1\%$ indicator bars.)

Figure 2 Heat capacities of water-formamide solutions at temperatures between 210 and 290 K, obtained from smoothed plots of raw C_p vs. T data at each composition indicated. Values may be compared with those of Visser et al.⁽⁶⁾ at 298.15 K. Connections between the 20 mol % solution and pure water data are indicated by dashed lines (for measurements in this difficult region see ref. 2). Natural extrapolations of solution data to 0% formamide are shown as full lines. Intercepts at $X = 0$ indicate "normal" component of C_p for pure water.

Figure 3 Expansion coefficients for water-formamide solutions at temperatures between 240 and 300 K. Alternative possible extrapolations to obtain the "normal" component of the water expansivity are indicated by dashed lines (see text for discussion of these alternatives).

Figure 4 Isothermal compressibilities, at the pressure of 10 MPa for water-formamide solutions at temperatures between 233 K and 293 K. Dashed lines indicate plausible extrapolations to obtain a

"normal" component of the compressibility of pure water.

- Figure 5** The "normal" component of the heat capacity, C_p of water obtained from extrapolations of Fig. 2 for the present water-formamide solution study. Comparisons are made with "normal" components obtained previously from $H_2O_2-H_2O$ and $N_2H_4-H_2O$ solution data.⁽²⁾ The figure compares these background components with the total C_p for water (see ref. 7).
- Figure 6** Plots of the "normal", "anomalous" and total (experimental) expansivities of water as a function of temperature. Curves (a), (b) and (c) indicate the consequences of different choices of binary solution composition range for extrapolations to 0 water content (see Fig. 3). "Anomalous" component suggested in ref. 3, is shown as a dashed line.
- Figure 7** Comparison of the total isothermal compressibility of water with the "normal" component of κ_T extracted from the present water-formamide solution data, and from the ethanol-water solution data (of ref. 1).
- Figure 8** Best fit of the "anomalous component" of C_p for water to Eq. (1) (curve a) and tests of Eq. (1) descriptions of the "anomalous" component of C_p for pure water. Curve (a) is an overall best fit, while curve (b) is a constrained best fit for an assigned value of γ , $\gamma = 1$.

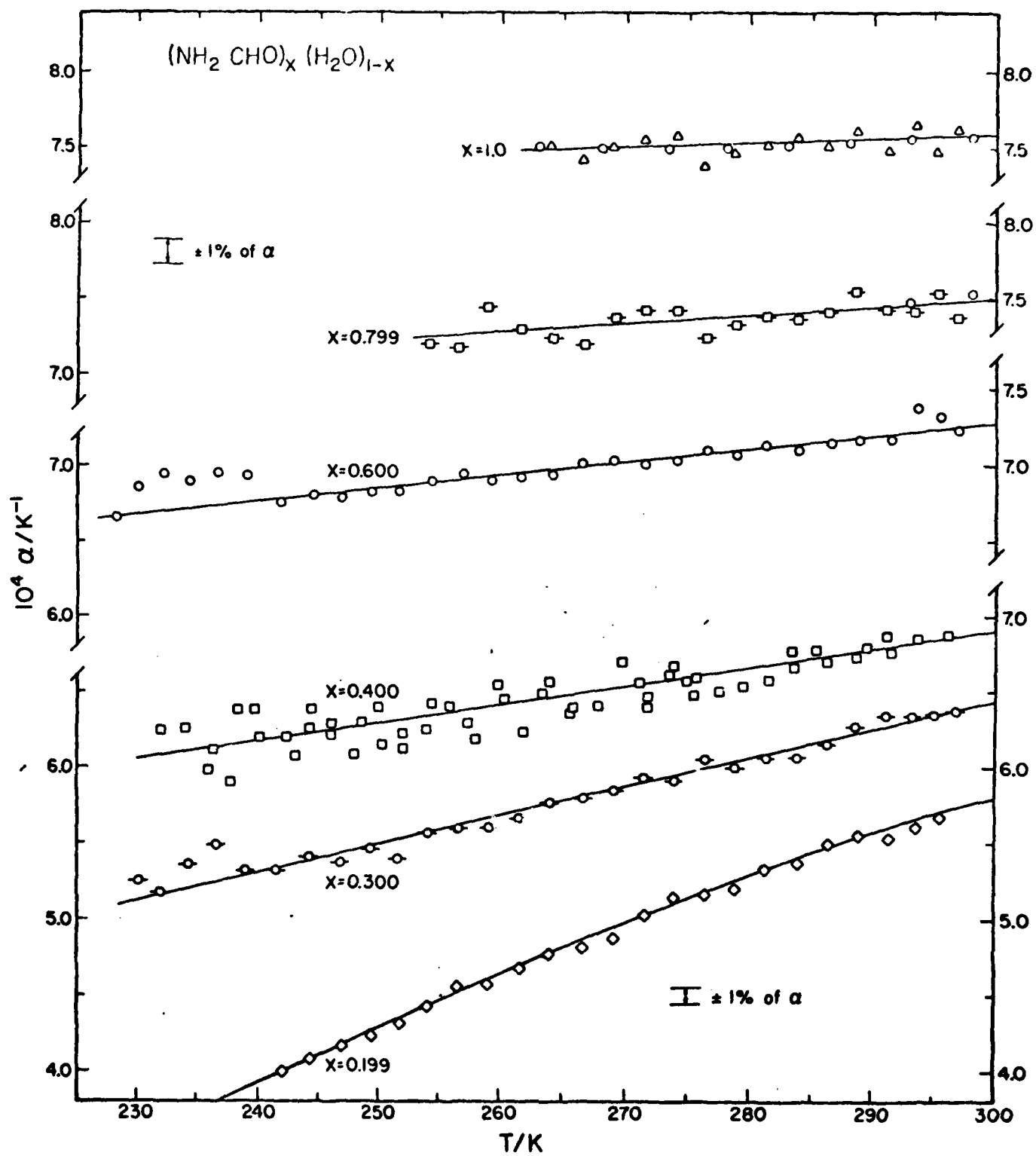
- Figure 9 (a) Overall best fits of the "anomalous" components of the expansion coefficient of pure water, using the three alternative "background" or "normal" component extrapolations discussed in the text. Comparisons indicate sensitivity of the γ parameter to the "background" form.
- (b) Constrained, $\gamma = 1$, best fits of anomalous component of the expansivity for the three different choices of background.

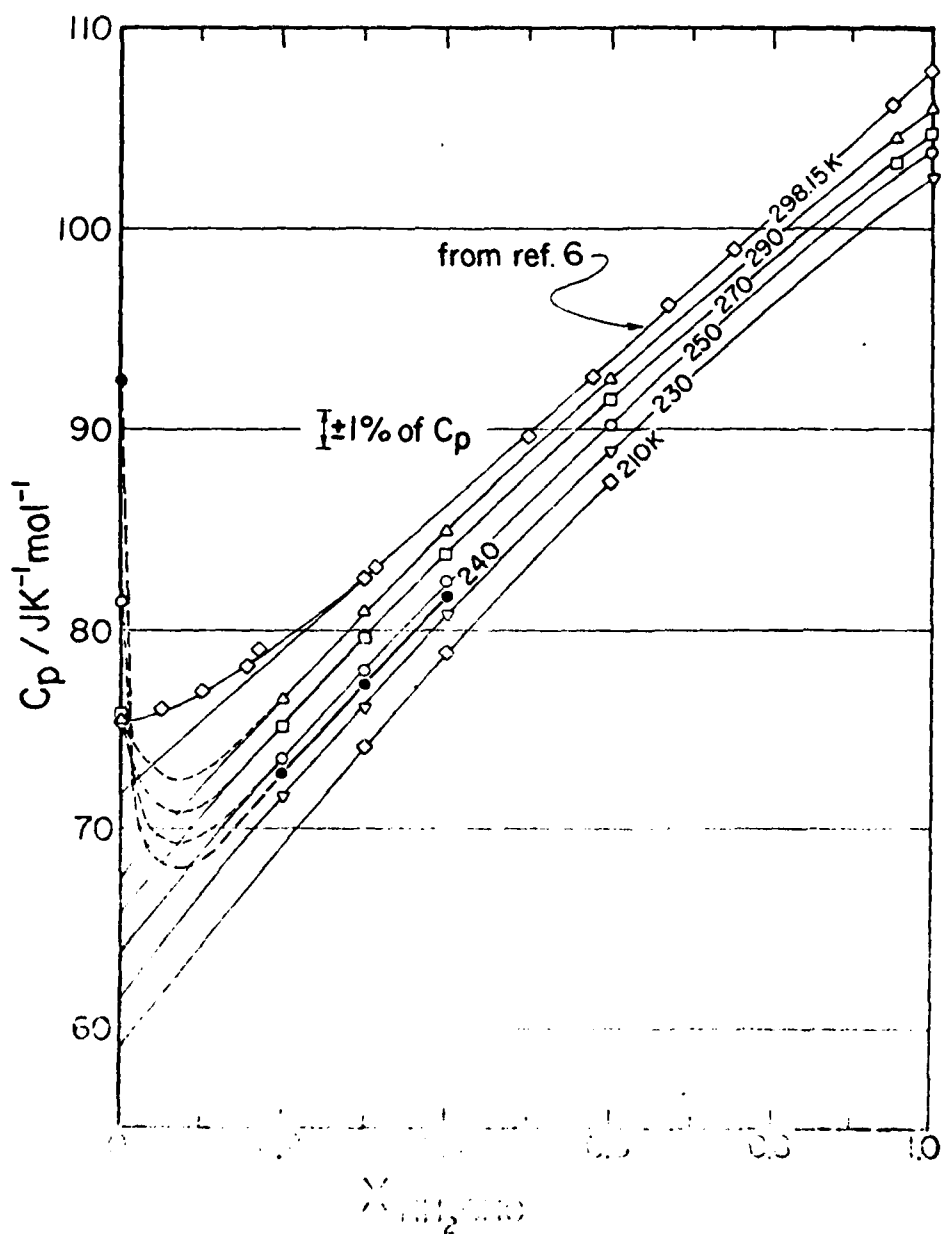
Figure 10 Plot of the constant volume heat capacity for water-formamide solutions assessed from combined data of this study.

Extrapolations to $X_{\text{NH}_2\text{CHO}} = 0$, yield a "normal" component of C_v for water.

Insert 1: "Normal" component of C_v for pure water compared with total C_v and total C_p for water. The lowest temperature C_v point is very uncertain, and low temperature form of C_v is probably asymptotic to the "normal" component. The crosses are C_v values calculated for a constant value of $V = 18.0$ cc/mole.

Insert 2: "Anomalous" component of C_v of water obtained from insert 1 by subtraction. Note Shottky anomaly form for this component.





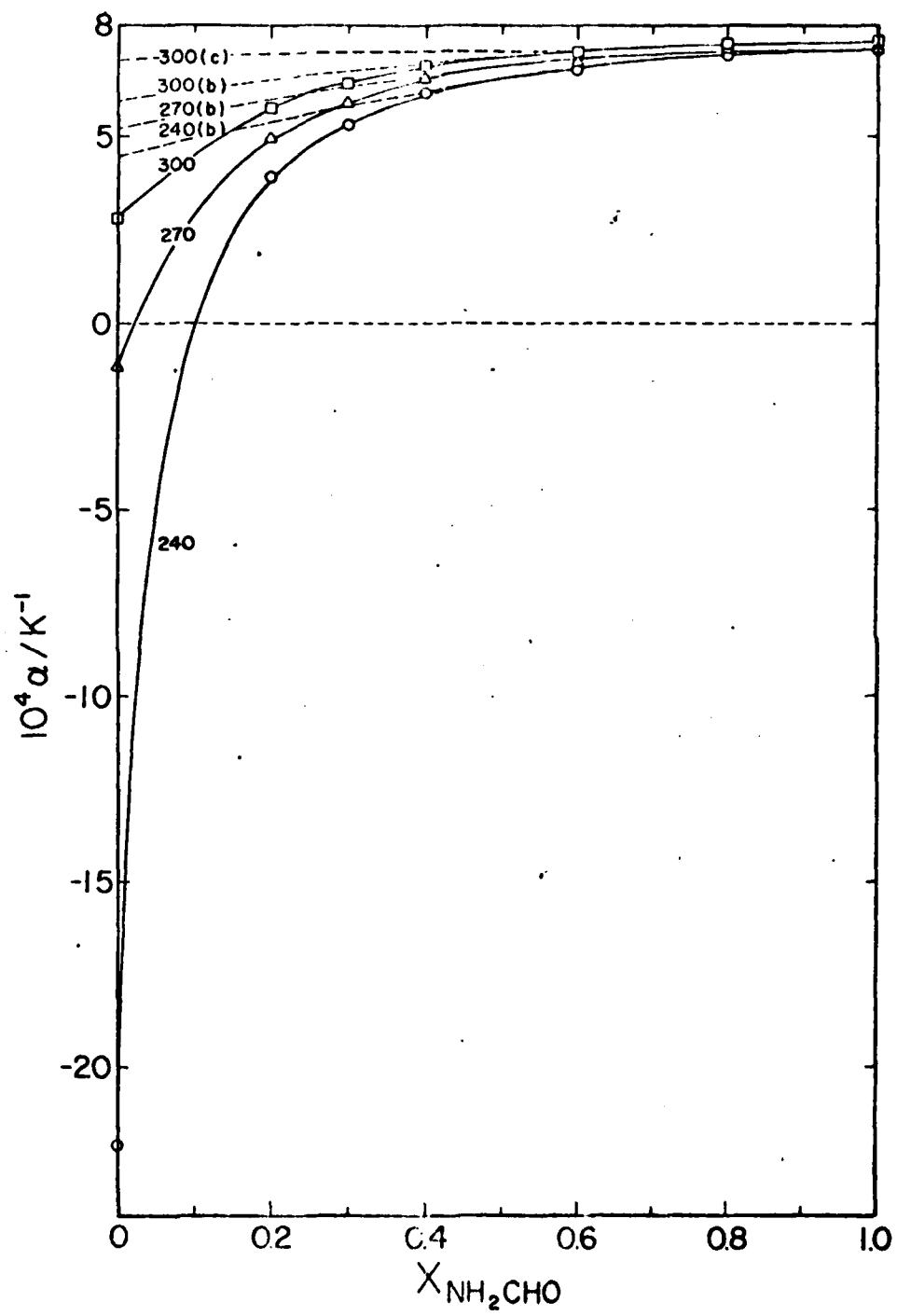
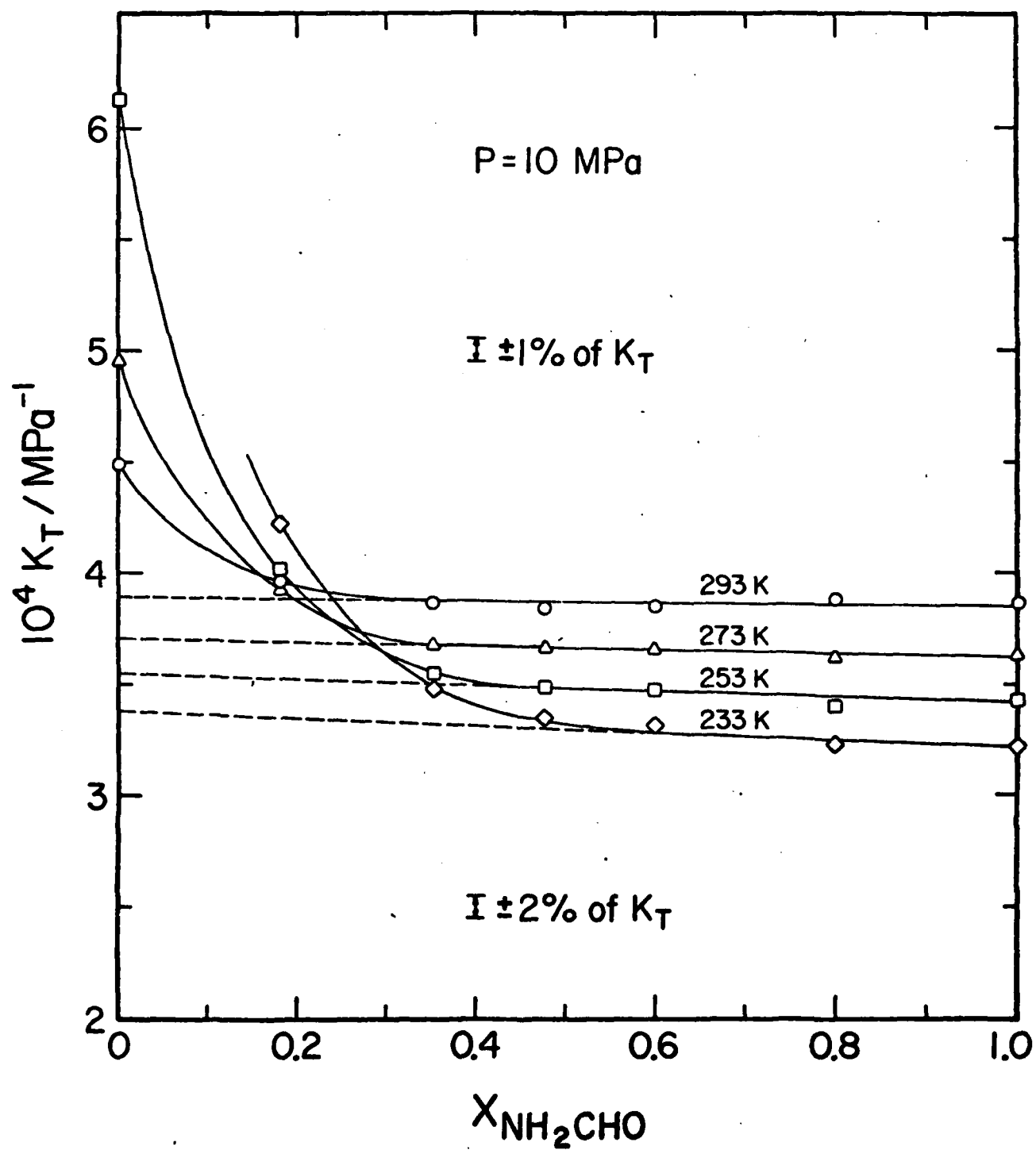
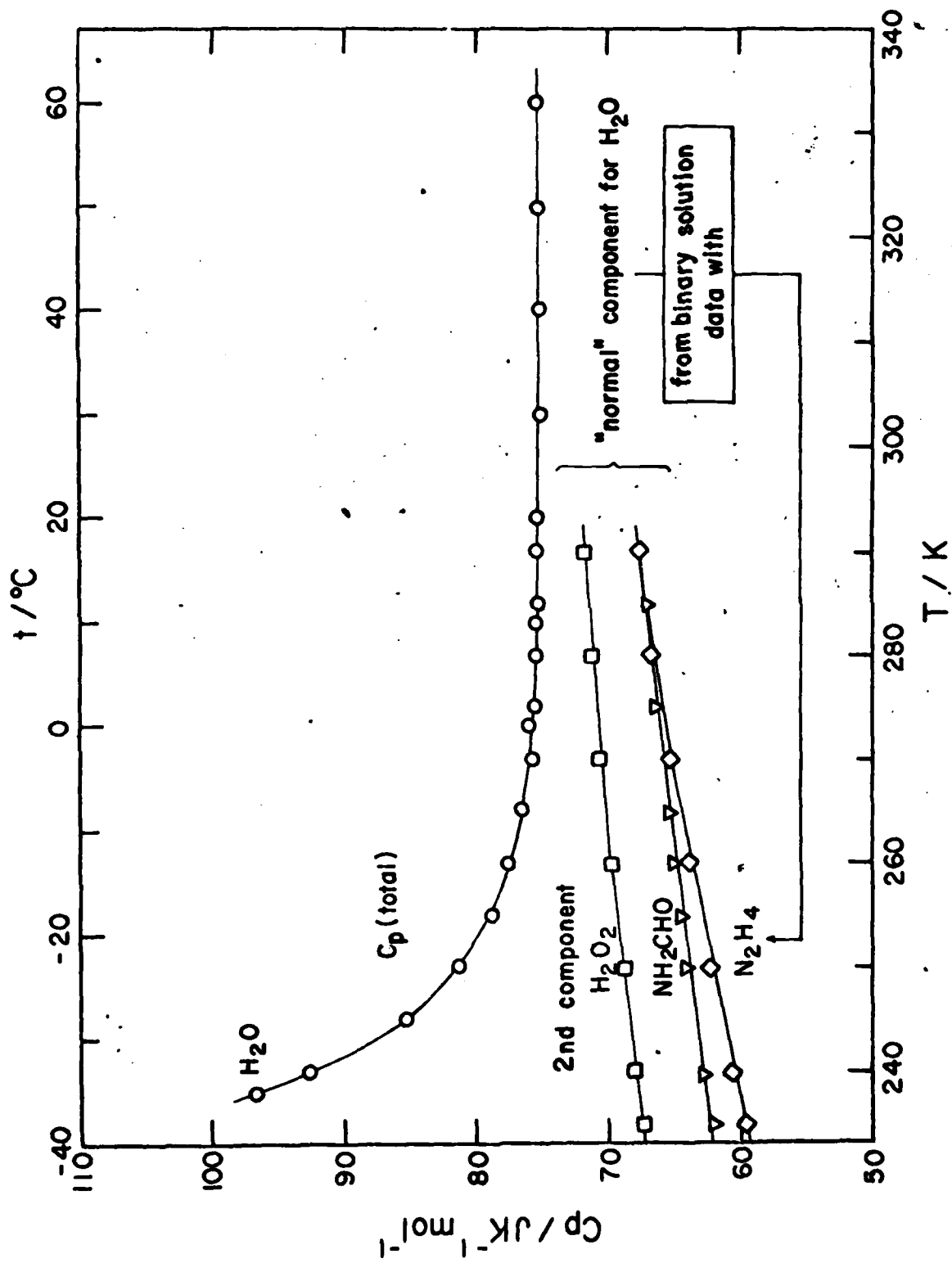
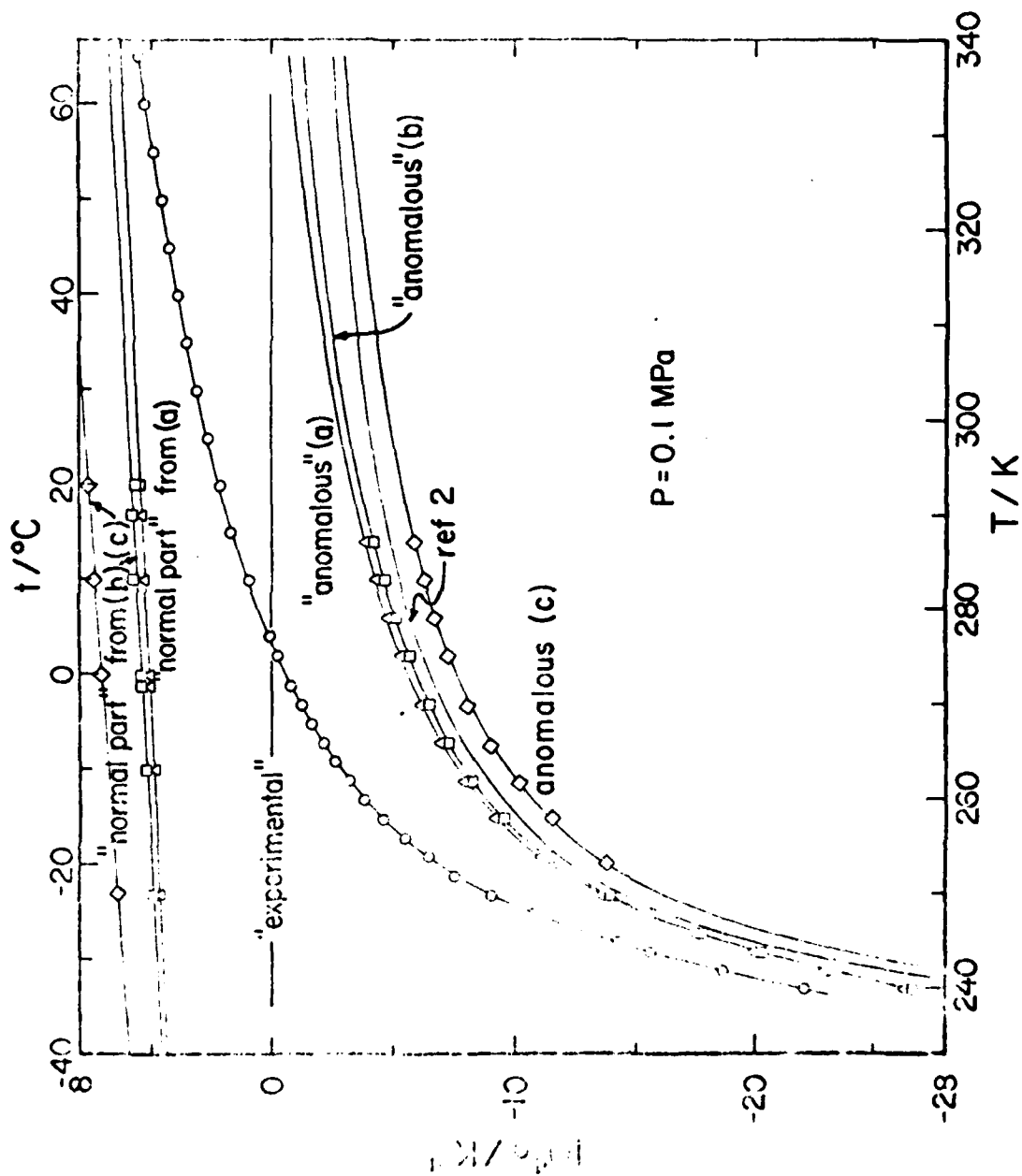
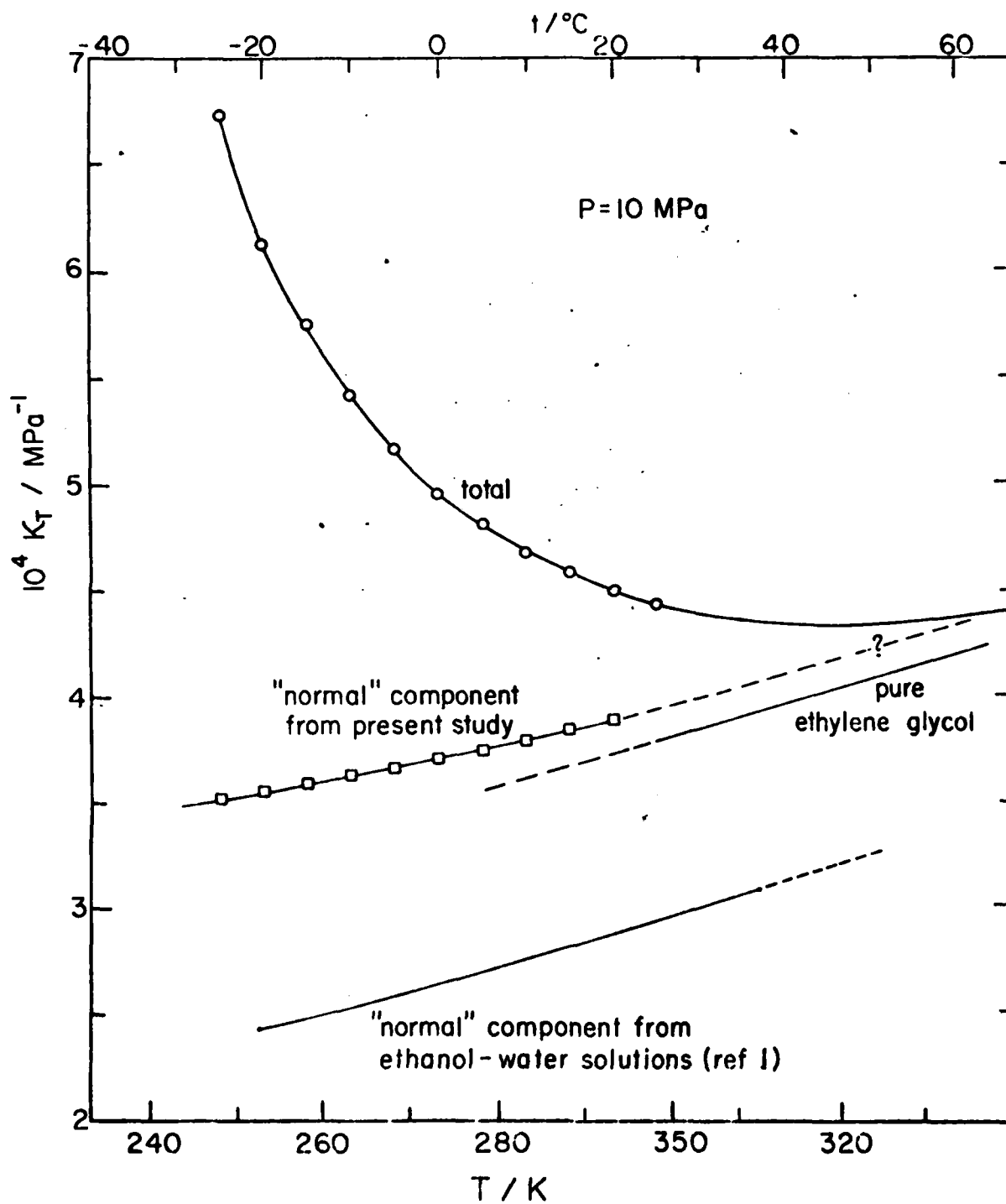


Fig. 3









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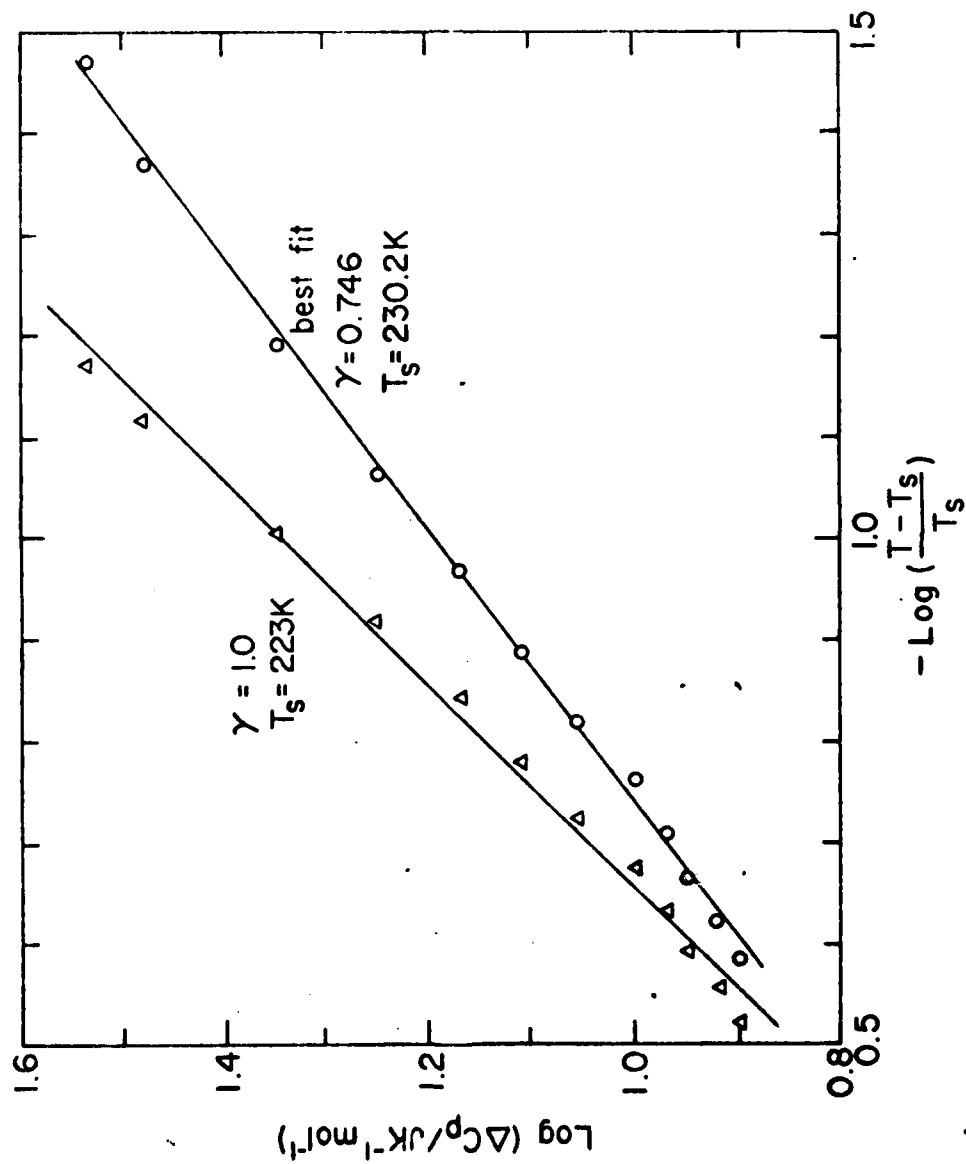
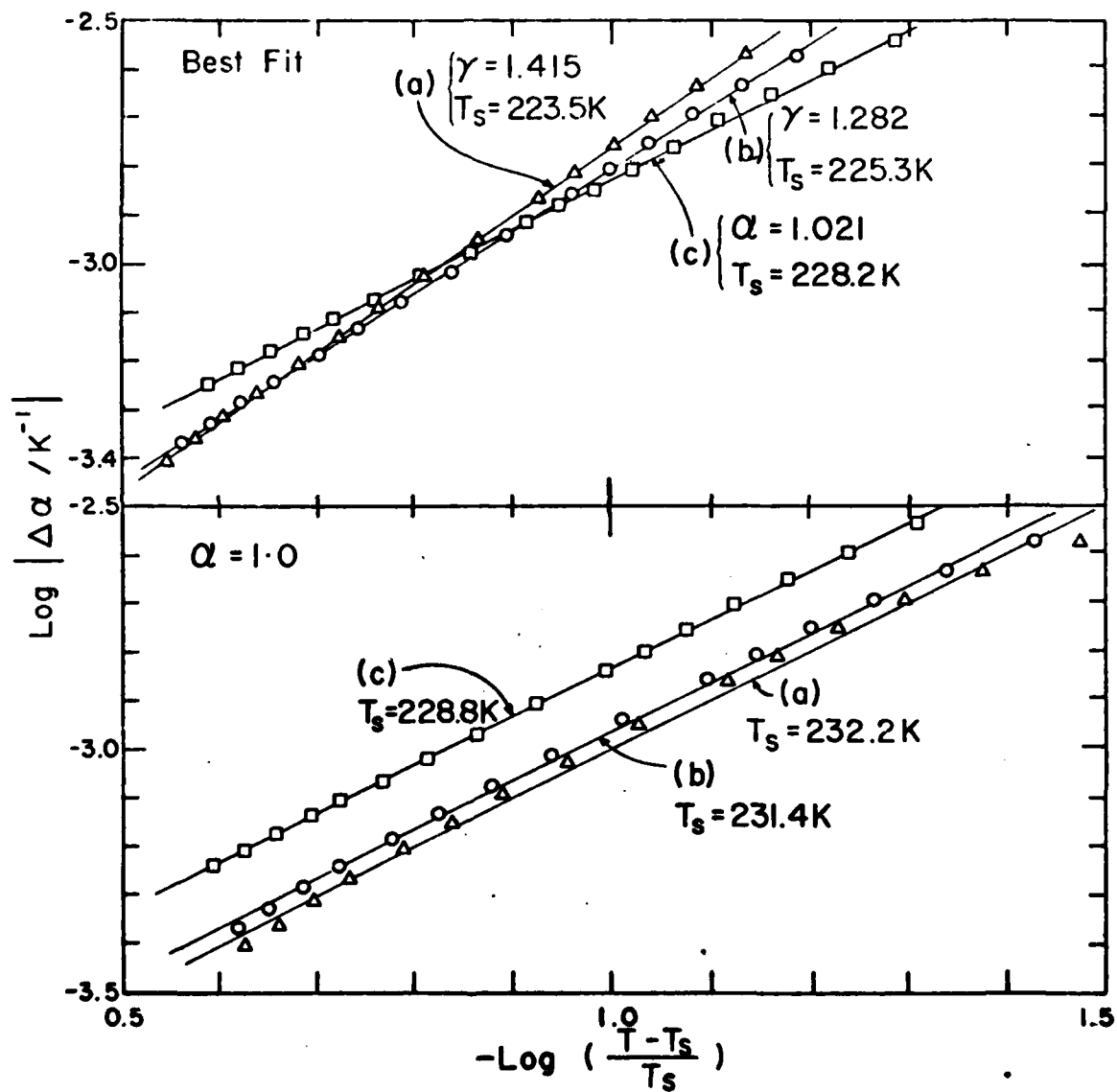
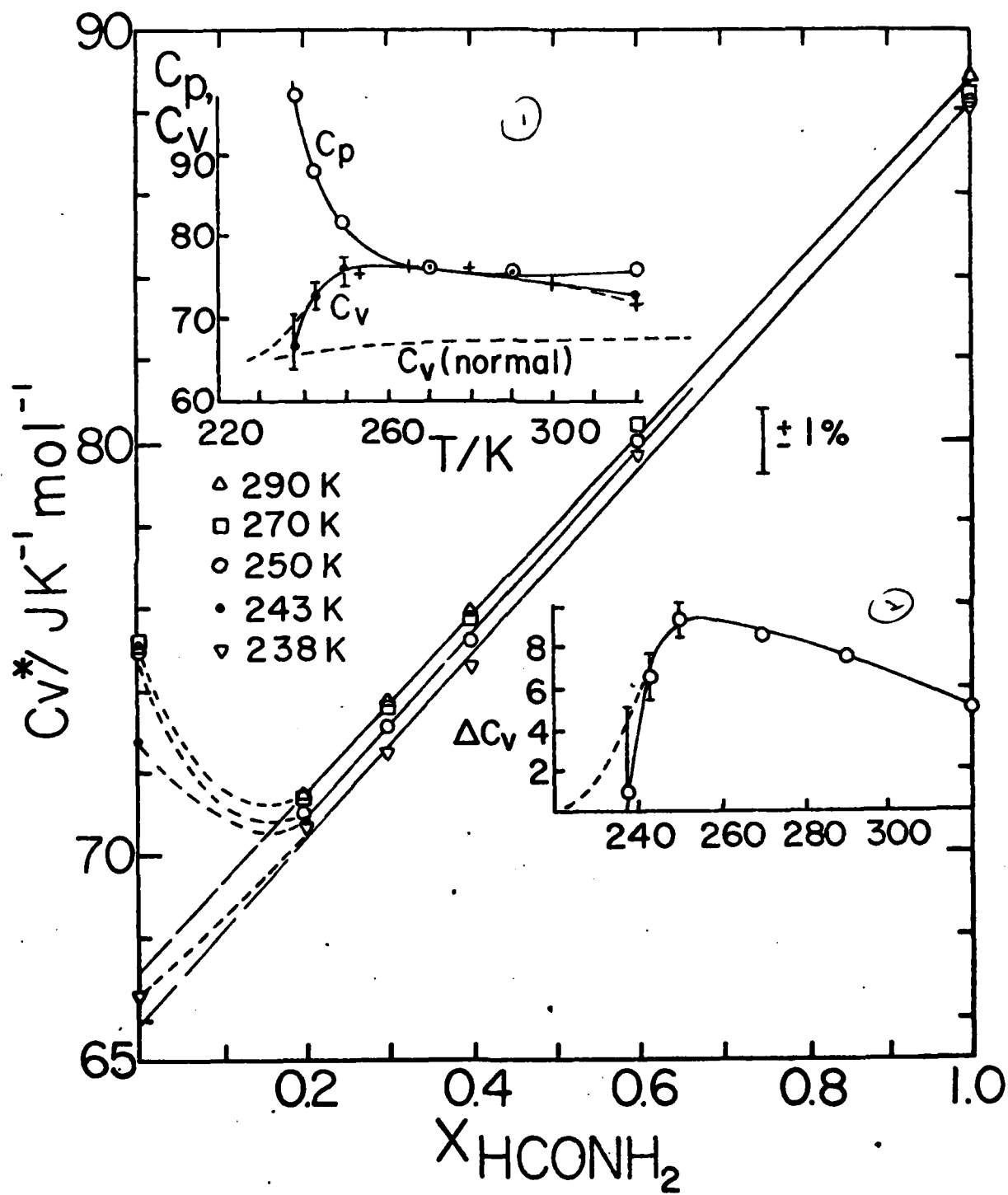


Fig. 8





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